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HIGH-PRESSURE ION-THERMAL PROPERTIES OF METALS
FROM AB INITIO INTERATOMIC POTENTIALS

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HIGH-PRESSURE ION-THERMAL PROPERTIES OF METALS FROM AB INITIO
INTERATOMIC POTENTIALS

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ABSTRACT

It has recently become possible for the first time to calculate ab initio two-ion and three-ion interatomic potentials in d-electron transition metals. The nature of these potentials for the 3d series metals is discussed. In the case of copper, where three-ion contributions may be neglected, application is made to the ion-thermal component of the equation of state and to the calculation of melting on the shock Hugoniot.

INTRODUCTION

Detailed knowledge about interatomic force laws in the condensed state represents an essential ingredient in a complete microscopic description of the materials properties of metallic solids and liquids. For example, interatomic potentials represent the primary physical input both in numerical simulations of materials properties by molecular dynamics and Monte Carlo techniques and in approximate calculations of the same by methods such as quasi-harmonic lattice dynamics in the solid and variational perturbation theory in the liquid. Heretofore, however, the first-principles theory of these potentials has only been developed for simple sp-bonded metals¹⁻⁵ (e.g., Al) and special limiting cases of d-electron metals near the beginning and end of the transition series (e.g., Ca and Zn).^{3,6} Recently, we have succeeded in extending this

capability to all d-electron transition metals,⁷ opening up many new avenues of application including high-pressure structural and thermal properties relevant to shocked materials.

INTERATOMIC POTENTIALS

For any homogeneous metal with a well-defined atomic volume Ω , the total energy of the system may be developed as a rigorous multi-ion expansion in terms of the individual ion or nuclear coordinates \underline{R}_i :

$$E_{\text{tot}}(\underline{R}_1, \dots, \underline{R}_N) = E_0(\Omega) + \frac{1}{2} \sum'_{i,j} v_2(R_{ij}) + \frac{1}{6} \sum'_{i,j,k} v_3(R_{ij}, R_{jk}, R_{ki}) + \dots \quad (1)$$

where E_0 , v_2 , v_3 , etc. are volume, two-ion, three-ion, etc. functionals, with $R_{ij} = |\underline{R}_i - \underline{R}_j|$, etc., and the primes exclude all self-interaction terms from the sums. The interatomic potentials are implicitly volume dependent, but explicitly structure independent, that is they do not depend on the absolute ion positions \underline{R}_i and are thus completely transferable at fixed volume. For nontransition metals it has been possible to obtain both E_0 and the central-force, pair potential v_2 in terms of appropriate nonlocal pseudopotentials.¹⁻⁶ Furthermore, the neglect of v_3 and higher potentials has proven to be an excellent approximation in most applications. For pure transition metals, on the other hand, not only are the individual functionals necessarily more complicated, but one expects a priori that the angular forces associated with the multi-ion terms to be more important due to the stronger scattering nature of the d electrons.

To treat the general problem of d-electron metals, it has been possible to synthesize pseudopotential methods for s and p electrons with tight-binding methods for d electrons into a generalized pseudopotential theory (GPT) applicable to both simple and transition metals.^{3,7} With regard to the total-energy expansion (1), however, the GPT has previously been developed only for the limiting cases of empty- and filled-d-band metals,³ where simplifying approximations are possible. We have now obtained explicit expressions for the volume, two-ion, and three-ion components of Eq. (1) in the partially-filled-d-band case applicable to transition metals. We have applied these results to the calculation of normal-density potentials across the entire 3d series and to copper from 40% expansion to about 3-fold compression. In the present paper, we shall concentrate primarily on the latter application; more details on the theory and the former application will be published elsewhere.⁷

Although the GPT itself becomes rather complex for transition metals, the nature of the resulting potentials can be fairly readily understood. The pair potential v_2 , for example, can be broken down as a sum of two major components. The first is a screened valence interaction analogous to what one encounters in simple metals. At sufficiently short distances, this reduces to a screened Coulomb repulsion between ions of charge Ze , where Z is the self-consistent valence of the metal, giving the average number of s and p electrons per atom. It turns out that Z is about 1.5 across the entire $3d$ series from Ca to Cu at normal density. In the case of copper, Z increases slowly with compression over the volume range we have considered, reaching a maximum value of about 2.2. The screened valence interaction at long range, on the other hand, has a slowly decaying oscillatory behavior, characteristic of metallic screening, where the wavelength of the oscillation decreases with increasing density. These short- and long-range features of v_2 are all clearly evident in Fig. 1 for copper.

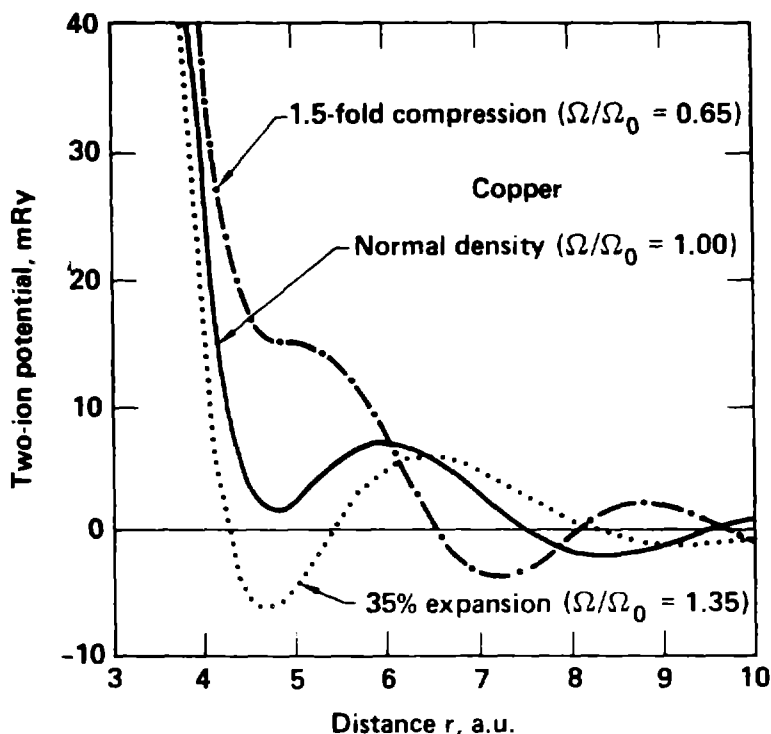


Fig. 1. GPT two-ion interatomic pair potential $v_2(r)$ in copper calculated at three different densities.

The second component of v_2 includes all remaining direct interactions between overlapping d -electron states. Near the center of the series, this represents a strong bonding attraction, corresponding to the increased cohesion for a half-filled d band, and a deep negative minimum in v_2 occurs in the vicinity of near neighbors. The depth of this minimum recedes rapidly as one goes towards either end of the series, and at the end of the series in copper is actually pushed to positive energy due the increased kinetic energy contribution of nearly-full overlapping d shells. This near-neighbor well is also strongly volume dependent, in copper being moved to still higher energy under compression and eventually becoming only a shoulder on a steep repulsive curve, as shown in Fig. 1.

The three-ion potential v_3 in transition metals is dominated by d -electron terms which are the counterparts of those contributing to second component of v_2 mentioned above. At the ends of the series (i.e., Ca and Cu), v_3 turns out to be essentially negligible, although near the center of the series, v_3 is rather strongly repulsive and quite essential to properly balance the large attractive component of v_2 . The fact that v_3 is negligible in copper makes this metal convenient for our present purposes, since calculating materials properties on the basis of Eq. (1) is then no more difficult than for simple metals.

APPLICATION TO SHOCK-COMPRESSED COPPER

We have investigated a number of materials properties of copper relevant to the shock-compressed state with our new interatomic potentials. The basic cohesive properties of this metal, which in the GPT depend on E_0 as well as v_2 in Eq. (1), are well described in comparison both to experiment and to more exact muffin-tin energy-band calculations,⁸ which employ no expansion of the total energy. This is demonstrated in Table I. At high pressure, on the other hand, the GPT zero-temperature isotherm becomes somewhat too soft relative to the corresponding muffin-tin result for this quantity.¹⁰ Important thermal properties such as phonons, the calculation of which is beyond current muffin-tin-band-theory capabilities, are obtained to about 10% accuracy in copper for individual modes at normal density with the present GPT pair potential. Phonon averages, however, such as the effective Debye temperature Θ_D and the Grüneisen constant γ , are, in this case at least, calculated more accurately, as also shown in Table I. (Here Θ_D is defined such that $9/8 k_B \Theta_D$ equals the zero-point vibrational energy.)

Table I. Zero-temperature cohesive energy (E_{coh}), equilibrium atomic volume (Ω_0), bulk modulus (B), and normal-density Debye temperature (Θ_D) and Grüneisen constant γ in copper.

	Muffin-tin band theory ^a	GPT	Experiment ^b
E_{coh} (Ry)	0.301	0.243	0.257
Ω_0 (a.u.)	77.5	77.0	78.9
B (Mbar)	1.55	1.50	1.42
Θ_D (K)	-	310	310
γ	-	2.1	2.0

^aRef. 8.

^bRef. 9.

We have further calculated the principal Hugoniot, treating separately the three components to the energy and pressure, e.g., for the pressure we take

$$P(\Omega, T) = P_0(\Omega) + P_{\text{ion}}(\Omega, T) + P_{\text{el}}(\Omega, T) , \quad (2)$$

where P_0 , P_{ion} , and P_{el} are the zero-temperature, ion-thermal, and electron-thermal partial pressures, respectively. For P_0 we have used the first-principles $T = 0$ muffin-tin-band-theory result¹⁰ mentioned above (which excludes the zero-point energy). The ion-thermal contribution has been calculated on the basis of our GPT pair potentials using quasi-harmonic lattice dynamics in the solid⁵ and variational perturbation theory, with Ross's soft-sphere reference system, in the liquid.^{5, 11} The electron-thermal contribution has been obtained from the low-temperature formula

$$P_{\text{el}}(\Omega, T) = \frac{\pi^2}{6} (k_B T)^2 \frac{d N(\epsilon_F)}{d\Omega} , \quad (3)$$

where $N(\epsilon_F)$ is the GPT-calculated density of states at the Fermi level ϵ_F . Our theoretical result is plotted in Fig. 2 and compared with the experimental two-stage light-gas-gun data of Mitchell and Nellis.¹² The agreement is clearly excellent and, indeed, is somewhat better than generally can be expected on the basis of uncertainties in the theory.

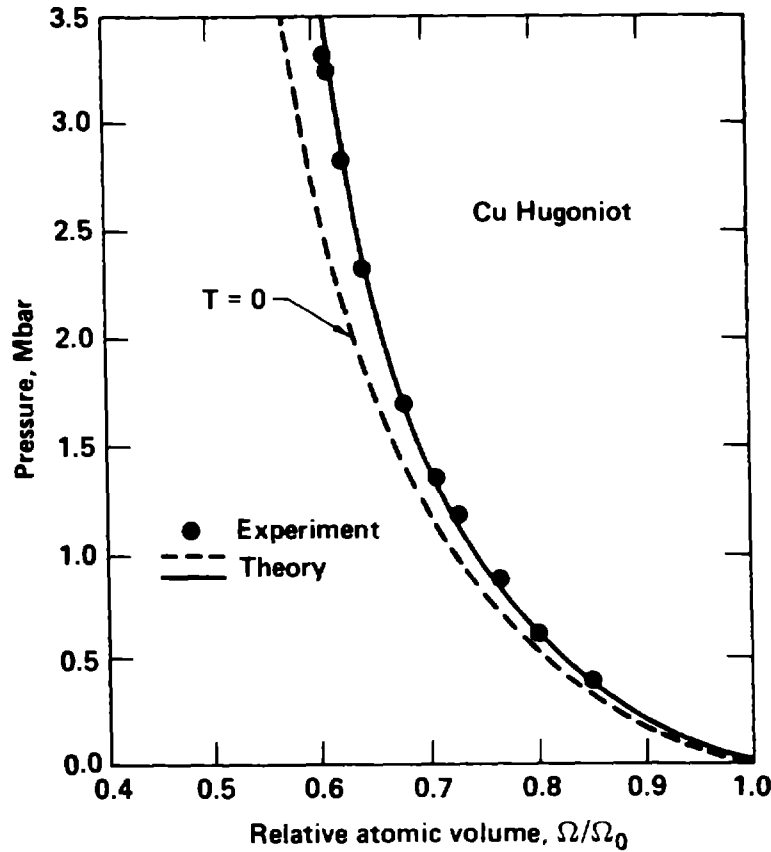


Fig. 2. First-principles theoretical Hugoniot (solid line) vs. experiment (solid dots, from Ref. 12) in copper. Zero-temperature isotherm (dashed line) is shown for comparison.

Finally, we have considered the question of melting on the Hugoniot. We have done a preliminary calculation of the melting curve in copper based on the location of the freezing line in the liquid. The latter is here approximated as the locus of points yielding a constant soft-sphere packing fraction η , as theoretically expected and as has been found to be true in the case of aluminum.⁵ We have used the value $\eta = 0.477$, which is consistent with both the observed zero-pressure melting temperature (1356 K) and the measured liquid structure factor.¹³ The calculated melting curve and its intersection with the Hugoniot are plotted in Fig. 3. The onset of melting is predicted to be at about 2.3 Mbar. Raising or lowering η by 0.025, respectively lowers or raises this prediction by about 0.3 Mbar.

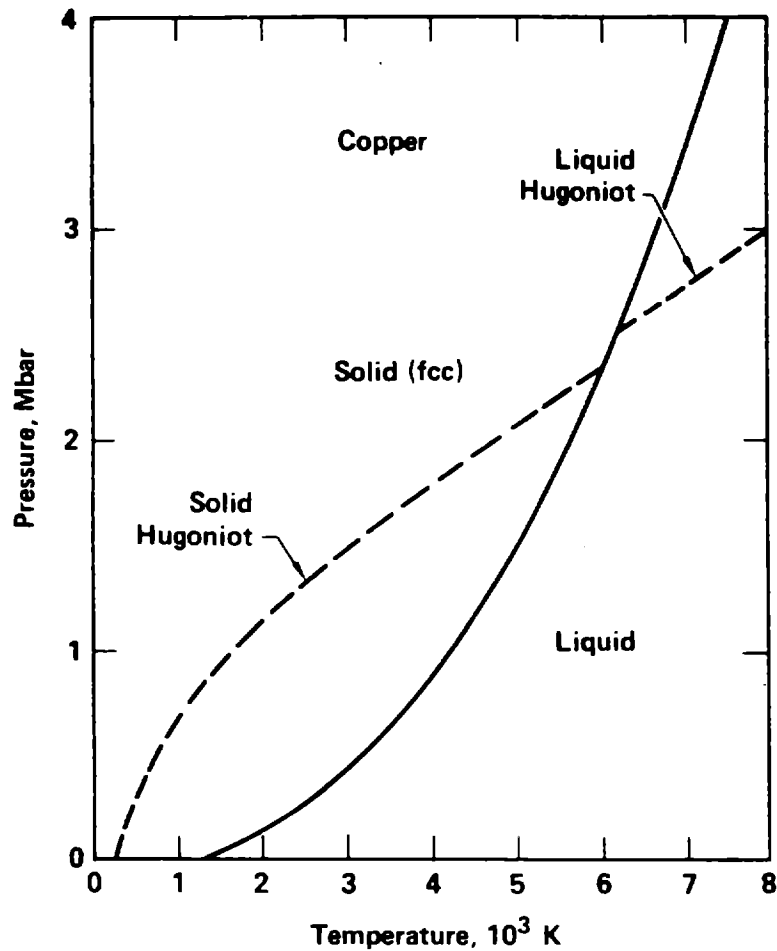


Fig. 3. Theoretical GPT melting curve (solid line) in copper and the predicted location of melting on the shock Hugoniot (dashed lines).

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